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(54) CATALYST FOR PURIFYING EXHAUST GAS AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To increase NOX purification performance in the lean atmosphere by incorporating at least one kind of noble metal selected from among platinum, rhodium and palladium, and ceria, barium and potassium on a refractory inorganic carrier and carrying a part or the whole of the noble metal on the ceria.

CONSTITUTION: A catalyst for purifying HC, CO and NOX contained in exhaust gas discharged from an internal combustion engine, especially the catalyst A in which purification performance of NOX is excellent in the oxygen excess atmosphere is formed by incorporating at least one kind of noble metal selected from a group consisting of platinum, rhodium and palladium, and ceria, barium and potassium on a refractory inorganic carrier and carrying a part or the whole of the noble metal on the ceria. In order to furthermore increase the NOX absorption action of the catalyst for purifying exhaust gas, at least two pieces of catalyst are provided in the exhaust gas current of the engine. The catalyst containing zeolite carrying copper is arranged on the upstream side for the exhaust gas current and the catalyst A is arranged on the downstream side therefor.

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CLAIMS

[Claim(s)]

[Claim 1] The catalyst for exhaust gas purification characterized by some or all of the noble metals concerned being supported by Seria including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, Seria, and barium and a potassium at least.

[Claim 2] The catalyst for exhaust-gas purification characterized by to consist of the catalyst bed B in which some or all of the noble metals concerned does not contain a potassium including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, Seria, and barium and a potassium at least, including a kind of noble metals chosen from the group which consists of the catalyst bed A currently supported by Seria, platinum, a rhodium, and palladium.

[Claim 3] The catalyst for exhaust gas purification characterized by establishing at least two catalysts into an engine exhaust air current, arranging a copper support zeolite content catalyst to the upstream to an exhaust air current, and arranging a catalyst according to claim 1 or 2 to the downstream.

[Claim 4] claims 1-3 -- the catalyst for exhaust gas purification to which Seria is characterized by being zirconium dissolution mold Seria in the catalyst for exhaust gas purification given [one of] in a term.

[Claim 5] claims 1-4 -- the catalyst for exhaust gas purification to which the content of a potassium and barium is converted into oxide weight, and per [catalyst 1L] and an each potassium are characterized by 0.1-20g, and barium being 0.1-100g in the catalyst for exhaust gas purification given [one of] in a term.

[Claim 6] The manufacture approach of the catalyst for exhaust gas purification characterized by calcinating after carrying out the coat of the alumina powder which supported at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium on fireproof inorganic support, and the Seria powder which supported some or all of the noble metals concerned to catalyst support, and calcinating after, sinking in the mixed water solution of the metal salt of a potassium and barium subsequently to this.

[Claim 7] The manufacture approach of the catalyst for exhaust gas purification which is characterized by making burning temperature into 300-600 degrees C in manufacturing the catalyst for exhaust gas purification according to claim 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the catalyst for exhaust gas purification which is especially excellent in the purification engine performance of NO_x under a hyperoxia ambient atmosphere, and its manufacture approach about the catalyst for exhaust gas purification which purifies the hydrocarbon (HC), the carbon monoxide (CO), and nitrogen oxides (NO_x) in the exhaust gas discharged by internal combustion engines, such as a gasoline and a Diesel motorcar, and a boiler, and its manufacture approach.

[0002]

[Description of the Prior Art] In recent years, from **** of the exhaustion problem of petroleum resources, and a global warming issue, implementation of a low-fuel-consumption automobile is expected and development of a lean combustion automobile is desired especially to the gasoline automobile. In a lean combustion automobile, the exhaust gas ambient atmosphere at the time of lean combustion transit turns into a hyperoxia ambient atmosphere ("lean atmosphere" is called hereafter) compared with a theoretical **** condition (a "SUTOIKI condition" is called hereafter). In lean atmosphere, when the conventional three way component catalyst was fitted, there was a problem that an NO_x cleaning effect became inadequate from the effect of superfluous oxygen. For this reason, development of the catalyst which can purify NO_x under a hyperoxia ambient atmosphere was desired.

[0003] Before, it is proposed, and various catalysts which raise the NO_x purification engine performance under lean atmosphere are divided roughly, and there are two kinds. One uses HC in exhaust gas as a reducing agent, and it oxidizes and NO_x is purified, and another absorbs NO_x under lean atmosphere and carries out emission purification of NO_x under a SUTOIKI condition or an overfuel (rich) ambient atmosphere.

[0004] As a former typical thing, the catalyst which made JP,63-100919,A support copper (Cu) to a zeolite is indicated, for example.

[0005] On the other hand, as a latter typical thing, JP,5-168860,A is made to support a lanthanum etc. to platinum (Pt), and the catalyst using a lanthanum as an NO_x absorber is indicated, for example.

[0006] However, the catalyst indicated by above-mentioned JP,5-168860,A has the problem that NO_x absorptance is inadequate, and the catalyst for exhaust gas purification which is the purpose which solves this problem, for example, uses alkali and alkaline earth metal for JP,5-261287,A, JP,5-317652,A, and JP,6-31139,A is indicated. Moreover, the catalyst for exhaust gas purification containing alkali metal, alkaline earth metal, a rare earth metal, and an iron-group metal is indicated by JP,6-142458,A.

[0007]

[Problem(s) to be Solved by the Invention] However, the above-mentioned conventional exhaust gas purification catalyst has the inadequate NO_x absorptivity ability under lean atmosphere, and is especially insufficient of the NO_x absorptivity ability after durability.

[0008] Moreover, although the function as a three way component catalyst is also required of coincidence since NO_x absorbed by lean atmosphere must be purified in SUTOIKI or a rich condition in the catalyst of such an NO_x absorption mold If the alkali of a considerable amount and alkaline earth metal are added in order to obtain sufficient NO_x absorption function, as mentioned above The strong basicity of alkali and alkaline earth metal affected the catalyst engine performance, the oxidation capacity of noble metals was reduced, and there was a problem that HC as a three way component catalyst and the inversion engine performance of CO became inadequate.

[0009] Therefore, the purpose of this invention is to offer the catalyst for exhaust gas purification which the NO_x purification engine performance under the lean atmosphere which did not show activity sufficient with

the conventional catalyst can be raised, and can fully discover the function as a three way component catalyst, and its manufacture approach.

[0010]

[Means for Solving the Problem] this invention persons reached [raising the NOx absorbing power under lean atmosphere, and] a header and this invention by including at least a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium, Seria, and barium and a potassium, as a result of inquiring in order to solve the above-mentioned technical problem.

[0011] The catalyst for exhaust gas purification according to claim 1 is characterized by some or all of the noble metals concerned being supported by Seria including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, Seria, and barium and a potassium at least.

[0012] In order to raise HC and CO activity of said catalyst further, moreover, the catalyst for exhaust gas purification according to claim 2 At least a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, The catalyst bed A with which some or all of the noble metals concerned is supported by Seria including Seria, and barium and a potassium It is characterized by consisting of the catalyst bed B which does not contain a potassium at least, including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium.

[0013] Furthermore, in order to raise further the NOx absorption of the catalyst for exhaust gas purification according to claim 1 or 2, the catalyst for exhaust gas purification according to claim 3 is characterized by establishing at least two catalysts into an engine exhaust air current, arranging a copper support zeolite content catalyst to the upstream to an exhaust air current, and arranging a catalyst according to claim 1 or 2 to the downstream.

[0014] in order [furthermore,] to raise further the NOx absorption and endurance of the catalyst for exhaust gas purification according to claim 1 to 3 -- the catalyst for exhaust gas purification according to claim 4 -- claims 1-3 -- in the catalyst for exhaust gas purification given [one of] in a term, Seria is characterized by being zirconium dissolution mold Seria.

[0015] in order [furthermore,] to raise the NOx absorptivity ability of the catalyst for exhaust gas purification according to claim 1 to 4 -- the catalyst for exhaust gas purification according to claim 5 -- claims 1-4 -- in the catalyst for exhaust gas purification given [one of] in a term, the content of a potassium and barium is converted into oxide weight, and per [catalyst 1L] and an each potassium are characterized by 0.1-20g, and barium being 0.1-100g.

[0016] At least one sort chosen from the group which consists of platinum, a rhodium, and palladium as noble metals used for the catalyst for exhaust gas purification of this invention is used. The content of said noble metals in a catalyst will not be limited especially if NOx absorbing power and the three way component catalyst engine performance at the time of SUTOIKI are fully obtained, but if fewer than 0.1g, even if the engine performance of 3 sufficient yuan will not be obtained but it will use it mostly from 10g, as for the significant improvement in a property, per [catalyst 1L / 0.1-10g] are desirable from the point of not seeing.

[0017] The base material for supporting some or all of said noble metals has the point of promotion of NOx oxidation reaction required for NOx absorption to desirable Seria. As noble-metals support base materials other than Seria, in order to secure the dispersibility of noble metals, especially the dispersibility of the noble metals after durability, a heat-resistant inorganic material with a large specific surface area is suitable, and especially an activated alumina is desirable. In order to raise a heat-resistant specific surface area, the activated alumina which added rare earth elements, a zirconia, etc. may be used. When the dispersibility of sufficient noble metals will not be acquired if there is less amount of the activated alumina used than per [catalyst 1L] and 50g, but it is mostly used from 300g, it is desirable that they are 50-300g from the point that degradation is seen.

[0018] Moreover, Seria used for the catalyst for exhaust gas purification of this invention has especially desirable zirconium dissolution mold Seria from the point which raises NOx oxidizing quality ability and endurance. As for "dissolution", some cerium atoms in Seria say the thing in the condition of having permuted by the zirconium, and the oxide of such a condition is also called a multiple oxide here. As for this zirconium dissolution mold Seria, it is desirable that a part or all of the component has compound-ized.

[0019] As for the amount of the Seria concerned, it is desirable that they are per [catalyst 1L / 10-100g]. If it is less than 10g, even if the engine performance or the NOx oxidation ability of 3 yuan will not fully be obtained but it will exceed 100g conversely, the capable increase-in-quantity effectiveness is not acquired. Moreover, although the zirconium of zirconium dissolution mold Seria and especially the ratio of a cerium

are not limited, it is desirable that mol % of a zirconium is 5 - 50%. When mol % of a zirconium becomes except said range, NO_x oxidation reaction required for NO_x absorption or thermal resistance will fall.

[0020] According to the structure where some or all of said noble metals is supported by Seria, NO_x oxidation reaction required for NO_x absorption increases further, and obtains the outstanding NO_x absorption.

[0021] Moreover, convert into metallic-oxide weight the content of the potassium used for the catalyst for exhaust gas purification of this invention, and barium, it catalyst 1L Hits, and it is desirable that a potassium is [0.1-20g, and barium] 0.1-100g respectively. Even if NO_x absorbing power is not fully acquired and it applies many amounts from this in case of an amount smaller than this, the capable increase-in-quantity effectiveness is not acquired.

[0022] Although the catalyst for exhaust gas purification according to claim 2 changes especially combining a catalyst bed A and the noble-metals catalyst bed B according to claim 1, arrangement of said A horizon and a B horizon is not limited especially from this thing [that the effectiveness of layer separation is accepted in the case of which], even if a B horizon is located in an A horizon lower layer at the upper layer, and even if reverse.

[0023] At least one sort of noble metals chosen from the group which consists of platinum, a rhodium, and palladium are contained in the noble metals in said noble-metals catalyst bed B. Moreover, if fewer than 0.1g, even if the engine performance of 3 sufficient yuan will not be obtained but it will use it mostly from 10g, as for the significant improvement in the engine performance, per [catalyst 1L / 0.1-10g] are desirable [the content of the noble metals will not be limited especially if NO_x absorbing power and the three way component catalyst engine performance at the time of SUTOIKI are fully obtained, but] from the point of not seeing. Moreover, a potassium must not be contained in the catalyst bed B concerned, and this is for not reducing the oxidation engine performance to HC and CO of noble metals, and maintaining highly.

[0024] In order to secure the dispersibility of noble metals, especially the dispersibility of the noble metals after durability to the base material for supporting the noble metals in the catalyst bed B concerned, a heat-resistant inorganic material with a large specific surface area is suitable, and especially an activated alumina is desirable. In order to raise a heat-resistant specific surface area, the activated alumina which added rare earth elements, a zirconia, etc. may be used. If there is less amount of the activated alumina used than per [catalyst 1L] and 50g, even if the engine performance will fall without acquiring the dispersibility of sufficient noble metals and it will use mostly from 300g, it is desirable that they are 50-300g from the point that degradation is seen.

[0025] Moreover, if fewer than 100g, even if sufficient NO_x reducibility ability will not be obtained but it will use it mostly from 300g, as for the significant improvement in the engine performance, per [catalyst support 1L / 100-300g] are desirable [especially if the content of Cu support zeolite catalyst prepared in the upstream to the exhaust gas style in invention according to claim 3 is an amount which shows an NO_x cleaning effect, it will not be limited, but] from the point of not seeing. In order to raise catalytic activity and endurance, Co, calcium, P, Ce, Nd, etc. may be added. That the activity after Cu ion exchange excels [that] in thermal resistance highly as a zeolite is used preferably, for example, there are a PENTARU mold zeolite, Y mold zeolite, mordenite, a ferrierite, etc.

[0026] The installation approach to the exhaust air system of the Cu support zeolite catalyst concerned and a catalyst according to claim 1 or 2 It is important to install a catalyst according to claim 1 or 2 in the upstream for Cu support zeolite catalyst to an exhaust gas style again at the downstream to an exhaust gas style. For example, the approach that the approach of equipping with and arranging two sorts of catalysts in one catalytic converter, the method of putting said two sorts of catalysts into a separate converter, and installing them, etc. are well-known can be used. Especially the installation location of a catalyst is not limited, for example, a manifold directly under location, an under floor location, etc. are raised. With the catalyst per the preceding paragraph of this catalyst system, and each latter part, when the purification engine performance is not enough, both the preceding paragraph, and both [either or] may be further made [two or more], or a variety catalyst may be added.

[0027] Honeycomb support, metal support, etc. which have the monolith structure which can use it, choosing suitably from well-known catalyst support as catalyst support used by this invention for example, which consists of a fireproof ingredient are mentioned. As for especially the configuration of this catalyst support, it is desirable to usually use it in a honeycomb configuration, although not restricted, it is possible also for using the honeycomb which consists of metallic materials, such as ferrite system stainless steel, although many things of quality of cordierite, such as a ceramic, are generally used as this honeycomb material, and may fabricate the catalyst powder itself in a honeycomb configuration further. By making the

configuration of a catalyst into the shape of a honeycomb, since the catalyst area of a catalyst and exhaust gas becomes large and pressure loss is also suppressed, when using as an object for automobiles etc., it is very advantageous.

[0028] In order to manufacture the catalyst for exhaust gas purification of this invention For example, prepare the compound of the element to support beforehand and the coat of the water-soluble slurry which ground such mixture with wet is carried out to monolith support. After drying, the coat of the components other than a potassium and barium is carried out to monolith support among the approach of calcinating and acquiring, and the element to support, after drying, it calcinates, and there is a method of sinking in and acquiring the water solubility which subsequently contains the salt of each component of a potassium and barium.

[0029] Especially the manufacture approach of the catalyst for exhaust gas purification according to claim 6 The alumina powder which supported at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium on fireproof inorganic support, It is characterized by calcinating, after carrying out the coat of the Seria powder which supported some or all of the noble metals concerned to catalyst support, and calcinating, after, sinking in the mixed water solution of the metal salt of a potassium and barium subsequently to this.

[0030] Moreover, in manufacturing the catalyst for exhaust gas purification according to claim 6, the manufacture approach of the catalyst for exhaust gas purification according to claim 7 is characterized by making burning temperature into 300-600 degrees C.

[0031] Although it can be used as a raw material compound for catalyst preparation combining a nitrate, a carbonate, ammonium salt, acetate, a halogenide, an oxide, etc., it is desirable to use a water-soluble salt especially from a viewpoint which raises the catalyst engine performance to HC and NOx. Unless it is not limited to an approach special as the method of preparation but is accompanied by the remarkable maldistribution of a component, various approaches, such as a well-known evaporation-to-dryness method, settling, and the sinking-in method, can be used.

[0032] There are an approach of calcinating and acquiring, after drying a cerium and the mixed water solution containing the salt of a zirconium, for example, although especially the manufacture approach especially of zirconium dissolution mold Seria is not limited, and the approach of calcinating, after drying the precipitate which added and obtained ammonium, the ammonium carbonate, and the citric acid in the mixed water solution of each salt.

[0033] Moreover, the above-mentioned heat treatment is performed under air or air circulation, and if 300 degrees C - 600 degrees C are desirable and is less than 300 degrees C, the whole will not serve as an oxide, but if it exceeds 600 degrees C, specific surface area will fall, and the burning temperature is not desirable.

[0034]

[Function] The catalyst for exhaust gas purification according to claim 1 contains at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium, Seria, and barium and a potassium, and when some or all of said noble metals is supported by Seria and both live together, it raises NOx oxidation reaction required for NOx absorption. Moreover, the NOx absorptance which barium and a potassium originally have is to be fully able to demonstrate because barium and a potassium touch the interface of noble metals and Seria. After durability makes it hard for these factors to lap, and to raise NOx absorbing power, and to fall the catalyst engine performance.

[0035] Especially the catalyst for exhaust gas purification according to claim 2 obtains sufficient three way component catalyst engine performance, obtaining NOx absorptivity ability by considering as the two-layer structure which comes to combine the catalyst bed A and the above-mentioned noble-metals support catalyst bed B containing the above-mentioned noble metals, Seria, and barium and a potassium. The noble metals in a catalyst bed A show the operation which mainly promotes absorption of NOx as described above. On the other hand, the noble metals in a catalyst bed B promote oxidation of HC and CO further, and raise the reduction effectiveness of NOx. Therefore, if a potassium is contained in a catalyst B horizon, in order that a potassium may reduce HC and CO oxidation engine performance of said noble metals, don't contain a potassium in the catalyst bed B concerned.

[0036] It is especially related with the catalyst for exhaust gas purification according to claim 3. Moreover, conventionally NOx purification catalysts, such as Cu support zeolite catalyst, and NOx absorption catalysts, such as Pt-lanthanum catalyst, for example, on the property, If the HC/NOx ratio in exhaust gas is small, a cleaning effect will not fully be acquired, and if Lean performs stationary transit in the latter, an NOx absorbed amount will reach saturation, and the former has the problem that absorption is lost soon, and was not able to purify NOx under the broad service condition. Therefore, invention according to claim 3 is

raising the absorption of a latter NO_x absorption catalyst by once contacting exhaust gas to Cu support zeolite catalyst. The absorption is oxidation of NO_x required for NO_x absorption at for example, Cu support zeolite catalyst having advanced promptly, and having assisted work of an NO_x absorber, and HC, NO_x and O₂ with Cu support zeolite catalyst convenient to NO_x absorption. It is possible that it has changed into concentration etc.

[0037] Furthermore, compared with the case where Seria purer than Seria is zirconium dissolution mold Seria is used, the NO_x oxidation engine performance and endurance increase, and especially the catalyst for exhaust gas purification according to claim 4 acquires the outstanding NO_x absorption and endurance.

[0038] Furthermore, especially the catalyst for exhaust gas purification according to claim 5 obtains NO_x absorptivity ability by limiting, as the content of a potassium and barium was respectively described above, securing the engine performance at the time of SUTOIKI.

[0039] Moreover, the manufacture approach of the catalyst for exhaust gas purification according to claim 6 The alumina powder which supported at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium on fireproof inorganic support, By considering as the process which calcinates after carrying out the coat of the Seria powder which supported some or all of the noble metals concerned to catalyst support, and is calcinated after, sinking in the mixed water solution of the metal salt of a potassium and barium subsequently to this A potassium and barium will touch the interface of noble metals and Seria, and the NO_x absorptance which barium and a potassium originally have can fully be demonstrated.

[0040] Moreover, the manufacture approach of the catalyst for exhaust gas purification according to claim 7 brings about the uniform dispersibility of noble metals into a catalyst, without spoiling the dispersibility of noble metals by limiting with 300-600 degrees C, as heat treatment burning temperature was described above.

[0041]

[Example] A following example and the following example of a comparison explain this invention.

The nitric-acid rhodium (Rh) water solution was sunk into example 1 activated-alumina powder, it calcinated at 400 degrees C after desiccation for 1 hour, and Rh support activated-alumina powder (powder A) was obtained. Rh concentration of this powder A was 2.0 % of the weight. After sinking in and drying a dinitro diamine platinum (Pt) water solution to activated-alumina powder, it calcinated at 400 degrees C for 1 hour, and Pt support activated-alumina powder (powder B) was obtained. Pt concentration of this powder B was 4.0 % of the weight. The 108g (powder A) of the above-mentioned Rh support activated-alumina powder, 531g (powder B) of Pt support activated-alumina powder, 180g of activity Seria powder, 81g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. Into the ingredient of the coat layer weight 100 g/L-support concerned, the mixed water solution of potassium acetate and barium acetate was calcinated at 400 degrees C for 1 hour, after sinking in and drying, and the catalyst for exhaust gas purification was acquired into it. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0042] The catalyst for exhaust gas purification was acquired like the example 1 except having converted the content of example 2 potassium and barium into the oxide respectively, and having made it into 10 g/L and 40 g/L.

[0043] Ammonia was added in the mixed water solution of example 3 zirconium nitrate and a cerium nitrate, obtained sediment was filtered, after drying, it calcinated at 400 degrees C for 3 hours, and zirconium dissolution mold Seria powder (powder C) was obtained. The amount of the zirconium contained in the zirconium dissolution mold Seria powder C concerned was converted into a metal mol, and were Zr/Ce=5/95. The catalyst for exhaust gas purification was acquired like the example 1 except having used this zirconium dissolution mold Seria powder C instead of the activity Seria powder of an example 1.

[0044] The zirconium dissolution mold Seria powder (powder D) of example 4 Zr/Ce=40/60 was obtained by the same approach as an example 3, and the catalyst for exhaust gas purification was acquired like the example 1 except having used this zirconium dissolution mold Seria powder D instead of the activity Seria powder of an example 1.

[0045] After sinking in and drying a dinitrodiammine platinum (Pt) water solution to example 5 activity Seria powder, it calcinated at 400 degrees C for 1 hour, and Pt support activity Seria powder (powder E) was

obtained. Pt concentration of this powder E was 2.0 % of the weight. 108g (powder A) of Rh support activated-alumina powder obtained in the example 1, 351g (powder B) of Pt support activated-alumina powder, the 180g (powder E) of the above-mentioned Pt support activity Seria powder, 261g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0046] The catalyst for exhaust gas purification was acquired like the example 5 except having used the zirconium dissolution mold Seria powder (powder C) obtained in the example 3 instead of the activity Seria powder of example 6 example 5.

[0047] 72g (powder A) of Rh support activated-alumina powder obtained in the example 7 example 1, 348g (powder B) of Pt support activated-alumina powder, 120g of activity Seria powder, 60g of activated-alumina powder, 124g of potassium acetate, 428g of barium acetate, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the lower layer catalyst of coat layer weight 75 g/L-support was acquired. The content of the potassium in the ingredient concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L. 108g (powder A) of Rh support activated-alumina powder obtained in the example 1, 540g (powder B) of Pt support activated-alumina powder, 180g of activity Seria powder, 72g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the above-mentioned 75 g/L-support, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and combining the upper catalyst and the lower layer catalyst, it was total and the catalyst for exhaust gas purification of coat layer weight 125 g/L-support was acquired.

[0048] The catalyst for exhaust gas purification was acquired like the example 7 except making reverse the upper and lower sides of a coat layer by making a lower layer catalyst into the upper catalyst, using the upper catalyst in example 8 example 7 as a lower layer catalyst.

[0049] 108g (powder A) of Rh support activated-alumina powder obtained in the example of comparison 1 example 1, 531g (powder B) of Pt support activated-alumina powder, 261g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0050] 108g (powder A) of Rh support activated-alumina powder obtained in the example of comparison 2 example 1, 531g (powder B) of Pt support activated-alumina powder, 180g of activity Seria powder, 81g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification of coat layer weight 100 g/L-support was acquired.

[0051] After sinking in and drying a dinitrodiammine palladium water solution to example 9 activated-alumina powder, it calcinated at 400 degrees C for 1 hour, and Pd support activated-alumina powder (powder F) was obtained. Pd concentration of this powder F was 4.0 % of the weight. The 630g (powder F) of the Pd support activated-alumina powder concerned, 180g of activity Seria powder, 90g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the

nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0052] The catalyst for exhaust gas purification was acquired like the example 9 except having converted the content of example 10 potassium and barium into the oxide respectively, and having made it into 10 g/L and 40 g/L.

[0053] The catalyst for exhaust gas purification was acquired like the example 9 except having used the zirconium dissolution mold Seria powder (powder C) obtained in the example 11 example 3 instead of the activity Seria powder of an example 9.

[0054] The catalyst for exhaust gas purification was acquired like the example 9 except having used the zirconium dissolution mold Seria powder (powder D) obtained in the example 12 example 4 instead of the activity Seria powder of an example 9.

[0055] After sinking in and drying a dinitrodiammine palladium water solution to example 13 activity Seria powder, it calcinated at 400 degrees C for 1 hour, and Pd support activity Seria powder (powder G) was obtained. Pd concentration of this powder G was 4.0 % of the weight. 450g (powder F) of Pd support activated-alumina powder obtained in the example 9, the 180g (powder G) of the above-mentioned Pd support activity Seria powder, 270g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst 15 concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0056] The catalyst for exhaust gas purification was acquired like the example 13 except having used the zirconium dissolution mold Seria powder (powder C) obtained in the example 14 example 3 instead of the activity Seria powder of an example 13.

[0057] 420g (powder F) of Pd support activated-alumina powder obtained in the example 15 example 9, 120g of activity Seria powder, 60g of activated-alumina powder, 124g of potassium acetate, 428g of barium acetate, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the lower layer catalyst of coat layer weight 75 g/L-support was acquired. The content of the potassium in the ingredient concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L. 630g (powder F) of Pd support activated-alumina powder obtained in the example 9, 180g of activity Seria powder, 90g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the above-mentioned 75 g/L-support, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and combining the upper catalyst and the lower layer catalyst, it was total and the catalyst for exhaust gas purification of 125 g/L-support was acquired.

[0058] The catalyst for exhaust gas purification was acquired like the example 15 except making reverse the upper and lower sides of a coat layer by making a lower layer catalyst into the upper catalyst, using the upper catalyst in example 16 example 15 as a lower layer catalyst.

[0059] Preferential grinding of 630g (powder F) of Pd support activated-alumina powder obtained in the example of comparison 3 example 9, 270g of activated-alumina powder, and the 900g of the water was added, thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support

concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0060] 630g (powder F) of Pd support activated-alumina powder obtained in the example of comparison 4 example 9, 180g of activity Seria powder, 90g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification of coat layer weight 100 g/L-support was acquired.

[0061] After repeating the activity filtered after mixing and stirring 5.2kg of copper-nitrate water solutions and 2kg of zeolite powder of 170.2 mols of examples, and L 3 times, it dried and calcinated and Cu support zeolite powder (powder H) was obtained. Cu concentration of this powder H was 5%. Preferential grinding of 810g [of this Cu support zeolite powder] (powder H) and silica sol (20% of solid content) 450g and the 540g of the water was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and Cu support zeolite catalyst of coat layer weight 300 g/L-support was acquired. The catalyst acquired in the example 1 in this Cu support zeolite catalyst by the upstream of exhaust air flow again has been arranged to the downstream.

[0062] The catalyst acquired in the example 2 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 18 example 17 has been arranged to the downstream.

[0063] The catalyst acquired in the example 3 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 19 example 17 has been arranged to the downstream.

[0064] The catalyst acquired in the example 4 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 20 example 17 has been arranged to the downstream.

[0065] The catalyst acquired in the example 5 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 21 example 17 has been arranged to the downstream.

[0066] The catalyst acquired in the example 6 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 22 example 17 has been arranged to the downstream.

[0067] The catalyst acquired in the example 7 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 23 example 17 has been arranged to the downstream.

[0068] The catalyst acquired in the example 8 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 24 example 17 has been arranged to the downstream.

[0069] The catalyst acquired in the example 9 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 25 example 17 has been arranged to the downstream.

[0070] The catalyst acquired in the example 10 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 26 example 17 has been arranged to the downstream.

[0071] The catalyst acquired in the example 11 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 27 example 17 has been arranged to the downstream.

[0072] The catalyst acquired in the example 12 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 28 example 17 has been arranged to the downstream.

[0073] The catalyst acquired in the example 13 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 29 example 17 has been arranged to the downstream.

[0074] The catalyst acquired in the example 14 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 30 example 17 has been arranged to the downstream.

[0075] The catalyst acquired in the example 15 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 31 example 17 has been arranged to the downstream.

[0076] The catalyst acquired in the example 16 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 32 example 17 has been arranged to the downstream.

[0077] The catalyst presentation of the above-mentioned examples 1-32 and the examples 1-4 of a comparison is shown in the next tables 1 and 2.

[Table 1]

	貴金属 (g/L)			添加材 (酸化物g/L)		
	P t	R h	P d	C e	K	B a
実施例 1	1.18	0.24	—	20.0	5.0	20.0
実施例 17	1.18	0.24	—	20.0	5.0	20.0
実施例 2	1.18	0.24	—	20.0	10.0	40.0
実施例 18	1.18	0.24	—	20.0	10.0	40.0
実施例 3	1.18	0.24	—	20.0	5.0	20.0
実施例 19	1.18	0.24	—	20.0	5.0	20.0
実施例 4	1.18	0.24	—	20.0	5.0	20.0
実施例 20	1.18	0.24	—	20.0	5.0	20.0
実施例 5	1.18	0.24	—	20.0	5.0	20.0
実施例 21	1.18	0.24	—	20.0	5.0	20.0
実施例 6	1.18	0.24	—	20.0	5.0	20.0
実施例 22	1.18	0.24	—	20.0	5.0	20.0
実施例 7	1.18	0.24	—	20.0	5.0	20.0
実施例 23	1.18	0.24	—	20.0	5.0	20.0
実施例 8	1.18	0.24	—	20.0	5.0	20.0
実施例 24	1.18	0.24	—	20.0	5.0	20.0
実施例 9	—	—	2.83	20.0	5.0	20.0
実施例 25	—	—	2.83	20.0	5.0	20.0
実施例 10	—	—	2.83	20.0	10.0	40.0
実施例 26	—	—	2.83	20.0	10.0	40.0
実施例 11	—	—	2.83	20.0	5.0	20.0
実施例 27	—	—	2.83	20.0	5.0	20.0
実施例 12	—	—	2.83	20.0	5.0	20.0
実施例 28	—	—	2.83	20.0	5.0	20.0
実施例 13	—	—	2.83	20.0	5.0	20.0
実施例 29	—	—	2.83	20.0	5.0	20.0
実施例 14	—	—	2.83	20.0	5.0	20.0
実施例 30	—	—	2.83	20.0	5.0	20.0
実施例 15	—	—	2.83	20.0	5.0	20.0
実施例 31	—	—	2.83	20.0	5.0	20.0
実施例 16	—	—	2.83	20.0	5.0	20.0
実施例 32	—	—	2.83	20.0	5.0	20.0

{*1} : Zr/Ceモル比 = 5/950

Table 2]

	貴金属 (g/L)			添加材 (g/L)		
	P t	R h	P d	C e	K	B a
比較例 1	1.18	0.24	—	—	5.0	20.0
比較例 2	1.18	0.24	—	20.0	—	—
比較例 3	—	—	2.83	—	10.0	10.0
比較例 4	—	—	2.83	20.0	—	—

[0078] About the catalyst and catalyst system of the example of trial 1 aforementioned examples 1-32, and the examples 1-4 of a comparison, catalytic activity evaluation after the first stage and durability was performed on condition that the following. The automatic evaluation equipment using the model gas which imitated the exhaust gas of an automobile was used for activity evaluation.

[0079] The durable condition engine 4400cc exhaust air system was equipped with the catalyst, at 600 degrees C, it operated for 50 hours and durability was performed.

[0080] Evaluation condition catalytic activity evaluation equips the exhaust air system of an engine with a displacement of 2000 cc with each catalyst. Operation for 30 seconds for 30 seconds by A/F=14.6 (SUTOIKI condition) after that A/F=22 (lean atmosphere) 1 cycle deed, The average invert ratio was measured respectively, the average invert ratio in this A/F=14.6 (SUTOIKI condition) and the average invert ratio in A/F=22 (lean atmosphere) were averaged, and it considered as the total invert ratio. This evaluation

was respectively performed after the first stage and durability, and the following formulas determined the catalytic activity evaluation value.

[Equation 1]

$$\text{NOx 転化率 (\%)} = \frac{(\text{触媒層入口 NOx 濃度}) - (\text{触媒層出口 NOx 濃度})}{(\text{触媒層入口 NOx 濃度})} \times 100$$

(H C, C O も同様)

[0081] The catalytic activity evaluation result obtained as a total invert ratio is shown in Tables 3-5. Compared with the example of a comparison, catalytic activity of the example was high and it was able to check the effectiveness of this invention mentioned later.

[Table 3]

	初期転化率 %			耐久後転化率 %		
	H C	C O	N O x	H C	C O	N O x
実施例 1	91	100	90	92	97	62
実施例 2	88	99	93	91	97	65
実施例 3	93	100	92	95	99	67
実施例 4	93	100	92	96	99	66
実施例 5	92	100	92	93	97	64
実施例 6	96	100	95	95	99	68
実施例 7	92	100	91	93	98	63
実施例 8	91	100	91	93	98	63
比較例 1	88	100	87	89	95	59
比較例 2	90	100	89	90	96	50

[Table 4]

	初期転化率 %			耐久後転化率 %		
	H C	C O	N O x	H C	C O	N O x
実施例 9	95	100	93	96	99	65
実施例 10	89	99	93	94	98	67
実施例 11	93	100	95	95	99	68
実施例 12	95	100	96	96	99	68
実施例 13	95	100	96	95	97	65
実施例 14	97	100	96	95	99	70
実施例 15	94	100	93	94	98	65
実施例 16	94	100	93	95	98	63
比較例 3	89	100	89	89	95	56
比較例 4	90	100	89	90	96	51

[Table 5]

	初期転化率 %			耐久後転化率 %		
	H C	C O	N O x	H C	C O	N O x
実施例17	92	100	98	92	98	77
実施例18	90	100	98	91	98	79
実施例19	93	100	96	95	99	78
実施例20	93	100	96	96	99	80
実施例21	92	100	97	93	97	82
実施例22	96	100	96	95	99	83
実施例23	92	100	98	93	98	79
実施例24	91	100	98	94	98	79
実施例25	96	100	97	90	95	79
実施例26	94	100	95	93	96	80
実施例27	95	100	96	96	99	80
実施例28	95	99	96	95	98	80
実施例29	96	100	98	96	99	83
実施例30	98	100	96	95	99	86
実施例31	95	100	96	95	98	80
実施例32	95	100	97	95	98	80

[0082]

[Effect of the Invention] When noble metals, Seria, and barium and a potassium are contained and some or all of noble metals is supported by Seria, the catalyst for exhaust gas purification according to claim 1 can raise the NOx purification engine performance under the lean atmosphere from which activity sufficient with the conventional catalyst is not acquired by raising NOx oxidation reaction required for NOx absorption, and can fully discover the function as a three way component catalyst after durability.

[0083] In addition to said effectiveness, the catalyst for exhaust gas purification according to claim 2 can raise HC and CO activity further by combining a noble-metals support layer and a catalyst bed according to claim 1 with arbitration up and down.

[0084] In addition to the above-mentioned effectiveness, the catalyst for exhaust gas purification according to claim 3 can raise NOx absorption further, when a copper support zeolite content catalyst is arranged to the upstream and it arranges a catalyst above-mentioned claim 1 or given in two to the downstream to an exhaust air current.

[0085] In addition to the above-mentioned effectiveness, the catalyst for exhaust gas purification according to claim 4 can raise the NOx oxidation engine performance and endurance further by making Seria into zirconium dissolution mold Seria further.

[0086] When the catalyst for exhaust gas purification according to claim 5 specifies the content of a potassium and barium further, in addition to the above-mentioned effectiveness, the engine performance at the time of SUTOIKI will also be secured.

[0087] By passing through the process which gave [above-mentioned] explanation, a potassium and barium can fully touch the interface of noble metals and Seria, and the manufacture approach of the catalyst for exhaust gas purification according to claim 6 can manufacture the catalyst for exhaust gas purification according to claim 1 which can fully demonstrate NOx absorptance by this simple.

[0088] In addition to the above-mentioned effectiveness, the manufacture approach of the catalyst for exhaust gas purification according to claim 7 can make homogeneity further distribution of the noble metals to the inside of the catalyst for exhaust gas purification by limiting heat treatment burning temperature further.

[Translation done.]



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**(54) CATALYST FOR PURIFYING EXHAUST GAS
 AND ITS PRODUCTION**

(57) Abstract:

PURPOSE: To increase NOX purification performance in the lean atmosphere by incorporating at least one kind of noble metal selected from among platinum, rhodium and palladium, and ceria, barium and potassium on a refractory inorganic carrier and carrying a part or the whole of the noble metal on the ceria.

CONSTITUTION: A catalyst for purifying HC, CO and NOX contained in exhaust gas discharged from an internal combustion engine, especially the catalyst A in which purification performance of NOX is excellent in

the oxygen excess atmosphere is formed by incorporating at least one kind of noble metal selected from a group consisting of platinum, rhodium and palladium, and ceria, barium and potassium on a refractory inorganic carrier and carrying a part or the whole of the noble metal on the ceria. In order to furthermore increase the NOX absorption action of the catalyst for purifying exhaust gas, at least two pieces of catalyst are provided in the exhaust gas current of the engine. The catalyst containing zeolite carrying copper is arranged on the upstream side for the exhaust gas current and the catalyst A is arranged on the downstream side therefor.

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最終頁に続く

(54)【発明の名称】 排気ガス浄化用触媒及びその製造方法

(57)【要約】

【目的】 従来の触媒では十分な活性を示さなかったリーン雰囲気下におけるNO_x浄化性能を向上させることができ、かつ三元触媒としての機能を十分に発現することができる排気ガス浄化用触媒及びその製造方法を提供する。

【構成】 耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持される。また、耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されている触媒層Aと、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属を含みかつカリウムを含有しない触媒層Bとから成る。更にエンジン排気気流中に触媒を少なくとも2個設け、排気気流に対して上流側に銅担持ゼオライト含有触媒を配置し、下流側に上記2種のいずれか一方の触媒を配置する。

【特許請求の範囲】

【請求項 1】 耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されていることを特徴とする排気ガス浄化用触媒。

【請求項 2】 耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されている触媒層 A と、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属を含みかつカリウムを含有しない触媒層 B とから成ることを特徴とする排気ガス浄化用触媒。

【請求項 3】 エンジン排気気流中に触媒を少なくとも 2 個設け、排気気流に対して上流側に銅担持ゼオライト含有触媒を配置し、下流側に請求項 1 又は 2 記載の触媒を配置することを特徴とする排気ガス浄化用触媒。

【請求項 4】 請求項 1～3 いずれかの項記載の排気ガス浄化用触媒において、セリアが、ジルコニウム固溶型セリアであることを特徴とする排気ガス浄化用触媒。

【請求項 5】 請求項 1～4 いずれかの項記載の排気ガス浄化用触媒において、カリウム及びバリウムの含有量は、酸化物重量に換算して、触媒 1 L あたり、各々カリウムが 0.1～20 g、バリウムが 0.1～100 g であることを特徴とする排気ガス浄化用触媒。

【請求項 6】 耐火性無機担体上に、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属を担持したアルミナ粉末と、当該貴金属の一部若しくは全部を担持したセリア粉末とを触媒担体にコートした後、焼成し、次いでこれにカリウム及びバリウムの金属塩の混合水溶液を含浸した後、焼成することを特徴とする排気ガス浄化用触媒の製造方法。

【請求項 7】 請求項 6 記載の排気ガス浄化用触媒を製造するにあたり、焼成温度を 300～600℃とすることを特徴とする排気ガス浄化用触媒の製造方法。

【発明の詳細な説明】**【0001】**

【産業上の利用分野】 本発明は、ガソリン及びディーゼル自動車、ボイラー等の内燃機関から排出される排気ガス中の炭化水素（HC）、一酸化炭素（CO）および窒素酸化物（NO_x）を浄化する排気ガス浄化用触媒及びその製造方法に関し、特に酸素過剰雰囲気下での NO_x の浄化性能に優れた排気ガス浄化用触媒及びその製造方法に関する。

【0002】

【従来の技術】 近年、石油資源の枯渇問題および地球温暖化問題の関点から、低燃費自動車の実現が期待されており、特にガソリン自動車に対しては希薄燃焼自動車の開発が望まれている。希薄燃焼自動車においては、希薄

燃焼走行時の排気ガス雰囲気は、理論空燃状態（以下、「ストイキ状態」と称す）に比べて酸素過剰雰囲気（以下、「リーン雰囲気」と称す）となる。リーン雰囲気において、従来の三元触媒を適応させた場合には、過剰な酸素の影響から NO_x 浄化作用が不十分となるという問題があった。このため酸素過剰雰囲気下においても NO_x を浄化できる触媒の開発が望まれていた。

【0003】 従来より、リーン雰囲気下における NO_x 浄化性能を向上させる触媒は種々提案されており、大別して 2 種類ある。一つは排気ガス中の HC を還元剤として NO_x を酸化して浄化するものであり、もう一つはリーン雰囲気下で NO_x を吸収し、ストイキ状態あるいは燃料過剰（リッチ）雰囲気下で NO_x を放出浄化するものである。

【0004】 前者の代表的なものとしては、例えば特開昭 63-100919 号公報に、銅（Cu）をゼオライトに担持させた触媒が開示されている。

【0005】 一方、後者の代表的なものとしては、例えば特開平 5-168860 号公報に、ランタン等を白金（Pt）に担持させてランタンを NO_x 吸収材として用いる触媒が開示されている。

【0006】 しかし上記特開平 5-168860 号公報に開示された触媒は、NO_x 吸収能力が不十分であるという問題があり、かかる問題を解決する目的で、例えば特開平 5-261287 号公報、特開平 5-317652 号公報及び特開平 6-31139 号公報にアルカリ、アルカリ土類金属を用いる排気ガス浄化用触媒が開示されている。また、特開平 6-142458 号公報には、アルカリ金属、アルカリ土類金属、希土類金属、鉄属金属を含有する排気ガス浄化用触媒が開示されている。

【0007】

【発明が解決しようとする課題】 しかしながら、上記従来の排気ガス浄化触媒は、リーン雰囲気下における NO_x 吸収性能が不十分であり、特に耐久後の NO_x 吸収性能が不足している。

【0008】 またこの様な NO_x 吸収型の触媒においては、リーン雰囲気中で吸収した NO_x をストイキあるいはリッチ状態時に浄化しなければならないので、三元触媒としての機能も同時に要求されるが、上述したように十分な NO_x 吸収機能を得るために相当量のアルカリ、アルカリ土類金属を添加すると、アルカリ、アルカリ土類金属の強い塩基性が触媒性能に影響を及ぼして貴金属の酸化能力を低下させ、三元触媒としての HC、CO の転化性能が不十分になるという問題があった。

【0009】 従って、本発明の目的は、従来の触媒では十分な活性を示さなかったリーン雰囲気下における NO_x 浄化性能を向上させることができ、かつ三元触媒としての機能を十分に発現することができる排気ガス浄化用触媒及びその製造方法を提供するにある。

【0010】

【課題を解決するための手段】本発明者らは、上記課題を解決するために研究した結果、白金、ロジウム及びパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウムとカリウムとを含むことにより、リーン雰囲気下での NO_x 吸収能を向上させることを見出し、本発明に到達した。

【0011】請求項1記載の排気ガス浄化用触媒は、耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されていることを特徴とする。

【0012】また前記触媒のHC及びCO活性を更に向上させるために、請求項2記載の排気ガス浄化用触媒は、耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されている触媒層Aと、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属を含みかつカリウムを含有しない触媒層Bとから成ることを特徴とする。

【0013】更に、請求項1又は2に記載の排気ガス浄化用触媒の NO_x 吸収作用を更に高めるために、請求項3記載の排気ガス浄化用触媒は、エンジン排気気流中に触媒を少なくとも2個設け、排気気流に対して上流側に銅担持ゼオライト含有触媒を配置し、下流側に請求項1又は2記載の触媒を配置することを特徴とする。

【0014】更に、請求項1～3に記載の排気ガス浄化用触媒の NO_x 吸収作用及び耐久性を更に高めるために、請求項4記載の排気ガス浄化用触媒は、請求項1～3いずれかの項記載の排気ガス浄化用触媒において、セリアが、ジルコニウム固溶型セリアであることを特徴とする。

【0015】更に、請求項1～4に記載の排気ガス浄化用触媒の NO_x 吸収性能を高めるために、請求項5記載の排気ガス浄化用触媒は、請求項1～4いずれかの項記載の排気ガス浄化用触媒において、カリウム及びバリウムの含有量は、酸化物重量に換算して、触媒1Lあたり、各々カリウムが0.1～20g、バリウムが0.1～100gであることを特徴とする。

【0016】本発明の排気ガス浄化用触媒に用いる貴金属としては、白金、ロジウムおよびパラジウムから成る群より選ばれる少なくとも1種が用いられる。触媒中の前記貴金属の含有量は、 NO_x 吸収能とストイキ時の三元触媒性能が十分に得られれば特に限定されないが、0.1gより少ないと十分な三元性能が得られず、10gより多く使用しても有意な特性向上はみられない点から触媒1Lあたり0.1～10gが好ましい。

【0017】前記貴金属の一部又は全部を担持するための基材は、 NO_x 吸収に必要な NO_x 酸化反応の促進の

点からセリアが好ましい。セリア以外の貴金属担持基材としては、貴金属の分散性、特に耐久後の貴金属の分散性を確保するため、比表面積の大きい耐熱性無機材料が適し、特に活性アルミナが好ましい。耐熱比表面積を高めるために希土類元素やジルコニア等を添加した活性アルミナを使用しても良い。活性アルミナの使用量は触媒1Lあたり、50gより少ないと十分な貴金属の分散性が得られず、300gより多く使用すると性能低下がみられる点から50～300gであることが好ましい。

10 【0018】また、本発明の排気ガス浄化用触媒に用いるセリアは、 NO_x 酸化性能及び耐久性を高める点から、特にジルコニウム固溶型セリアが好ましい。ここで「固溶」とは、セリア中のセリウム原子の一部がジルコニウムと置換した状態のことをいい、このような状態の酸化物は複合酸化物とも称される。該ジルコニウム固溶型セリアは、その成分の一部若しくは全部が複合化していることが好ましい。

20 【0019】当該セリアの量は触媒1Lあたり10～100gであることが好ましい。10g未満だと三元性能もしくは NO_x 酸化能が十分に得られず、逆に100gを超えても有為な増量効果は得られない。またジルコニウム固溶型セリアのジルコニウムとセリウムの比率は特に限定されないが、ジルコニウムのモル%が5～50%であることが好ましい。ジルコニウムのモル%が前記範囲以外となると、 NO_x 吸収作用に必要な NO_x 酸化反応、あるいは耐熱性が低下することとなる。

【0020】前記貴金属の一部もしくは全部がセリアに担持される構造により、 NO_x 吸収に必要な NO_x 酸化反応が更に高まり、優れた NO_x 吸収作用を得る。

30 【0021】また、本発明の排気ガス浄化用触媒に用いるカリウム及びバリウムの含有量は、金属酸化物重量に換算して、触媒1Lあたり各々カリウムが0.1～20g、バリウムが0.1～100gであることが好ましい。これより少ない量だと NO_x 吸収能が十分に得られず、またこれより多い量を加えても有為な増量効果は得られない。

40 【0022】特に、請求項2記載の排気ガス浄化用触媒は、請求項1記載の触媒層Aと、貴金属触媒層Bとを組み合わせるが、前記A層及びB層の配置は、上層にA層下層にB層が位置しても、またこの逆であっても、いずれの場合においても層分離の効果が認められることから特に限定されない。

50 【0023】前記貴金属触媒層B中の貴金属には、白金、ロジウム及びパラジウムから成る群より選ばれる少なくとも1種の貴金属が含まれる。またその貴金属の含有量は、 NO_x 吸収能とストイキ時の三元触媒性能が十分に得られれば特に限定されないが、0.1gより少ないと十分な三元性能が得られず、10gより多く使用しても有意な性能向上はみられない点から触媒1Lあたり0.1～10gが好ましい。また当該触媒層B中にはカ

リウムを含有してはならず、これは貴金属のH C及びC Oに対する酸化性能を低下させず高く維持するためである。

【0024】当該触媒層B中の貴金属を担持するための基材には貴金属の分散性、特に耐久後の貴金属の分散性を確保するため、比表面積の大きい耐熱性無機材料が適し、特に活性アルミナが好ましい。耐熱比表面積を高めるために希土類元素やジルコニア等を添加した活性アルミナを使用しても良い。活性アルミナの使用量は触媒1 Lあたり、50 gより少ないと十分な貴金属の分散性が得られずに性能が低下し、300 gより多く用いても性能低下がみられる点から50～300 gであることが好ましい。

【0025】また、請求項3記載の発明において、排気ガス流に対して上流側に設けられたCu担持ゼオライト触媒の含有量は、NO_x浄化作用を示す量であれば特に限定されないが、100 gより少ないと十分なNO_x還元性能が得られず、300 gより多く使用しても有意な性能向上はみられない点から触媒担体1 Lあたり100～300 gが好ましい。触媒活性及び耐久性を向上させるために、例えばCo, Ca, P, Ce, Nd等を添加してもよい。ゼオライトとしては、Cuイオン交換後の活性が高くかつ耐熱性に優れるものが好ましく使用され、例えば、ペンタル型ゼオライト、Y型ゼオライト、モルデナイト、フェリエライト等がある。

【0026】当該Cu担持ゼオライト触媒と、請求項1又は2記載の触媒の排気系への設置方法は、Cu担持ゼオライト触媒を排気ガス流に対して上流側に、また請求項1又は2記載の触媒を排気ガス流に対して下流側に設置することが重要であり、例えば1個の触媒コンバータ内に2種の触媒を装着して配置する方法や、前記2種の触媒を別々のコンバータに入れて設置する方法等の公知の方法を用いることができる。触媒の設置位置は特に限定されず、例えばマニホールド直下位置や床下位置等があげられる。この触媒系の前段、後段それぞれ1個ずつの触媒で浄化性能が十分でない場合には、さらに前段、後段の何れかあるいは両方を複数個としたり、多種触媒を追加しても良い。

【0027】本発明で用いられる触媒担体としては、公知の触媒担体の中から適宜選択して使用することができ、例えば耐火性材料からなるモノリス構造を有するハニカム担体やメタル担体等が挙げられる。この触媒担体の形状は、特に制限されないが、通常はハニカム形状で使用することが好ましく、このハニカム材料としては、一般にセラミック等のコージュライト質のものが多く用いられるが、フェライト系ステンレス等の金属材料からなるハニカムを用いることも可能であり、更には触媒粉末そのものをハニカム形状に成形しても良い。触媒の形状をハニカム状とすることにより、触媒と排気ガスの触媒面積が大きくなり、圧力損失も抑えられるため自動車

用等として用いる場合に極めて有利である。

【0028】本発明の排気ガス浄化用触媒を製造するには、例えば担持する元素の化合物を予め用意し、これらの混合物を湿式にて粉碎した水溶性スラリーをモノリス担体にコートし、乾燥した後焼成して得る方法、また、担持する元素のうちカリウム及びバリウム以外の成分をモノリス担体にコートし、乾燥した後焼成し、次いでカリウム及びバリウムの各成分の塩を含有する水溶性を含浸して得る方法がある。

【0029】特に、請求項6記載の排気ガス浄化用触媒の製造方法は、耐火性無機担体上に、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属を担持したアルミナ粉末と、当該貴金属の一部若しくは全部を担持したセリア粉末とを触媒担体にコートした後、焼成し、次いでこれにカリウム及びバリウムの金属塩の混合水溶液を含浸した後、焼成することを特徴とする。

【0030】また、請求項7記載の排気ガス浄化用触媒の製造方法は、請求項6記載の排気ガス浄化用触媒を製造するにあたり、焼成温度を300～600℃とすることを特徴とする。

【0031】触媒調製用原料化合物としては、硝酸塩、炭酸塩、アンモニウム塩、酢酸塩、ハロゲン化物、酸化物等を組み合わせて使用することができるが、特に水溶性の塩を使用することがH C及びNO_xに対する触媒性能を向上させる観点から好ましい。調製法としては特殊な方法に限定されず、成分の著しい偏在を伴わない限り、公知の蒸発乾固法、沈殿法、含浸法等の種々の方法を用いることができる。

【0032】特に、ジルコニウム固溶型セリアの製造方法は特に限定されないが、例えば、セリウム、ジルコニウムの塩を含む混合水溶液を乾燥した後、焼成して得る方法や、それぞれの塩の混合水溶液にアンモニウムや炭酸アンモニウムやクエン酸を添加して得た沈殿物を乾燥した後、焼成する方法がある。

【0033】また、上記熱処理は、空気又は空気流通下で行ない、その焼成温度は、300℃～600℃が好ましく、300℃未満だと全体が酸化物とならず、600℃を超えると比表面積が低下し、望ましくない。

【0034】

【作用】請求項1記載の排気ガス浄化用触媒は、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含有し、前記貴金属の一部又は全部がセリアに担持されて両者が共存することにより、NO_x吸収に必要なNO_x酸化反応を向上させる。またバリウム及びカリウムとが、貴金属とセリアとの界面に接することで、バリウム及びカリウムとが本来有するNO_x吸収能力が十分に発揮できることとなっている。これらの要因が重なって、NO_x吸収能を高め、かつ耐久後も触媒性能を低下

しにくくしている。

【0035】特に、請求項2記載の排気ガス浄化用触媒は、上記貴金属と、セリアと、バリウム及びカリウムとを含有する触媒層Aと上記貴金属担持触媒層Bとを組み合わせる二層構造とすることにより、 NO_x 吸収性能を得ながら、十分な三元触媒性能を得る。触媒層A中の貴金属は、上記したように主に NO_x の吸収を促進させる作用を示すものである。一方触媒層B中の貴金属は、更にHC及びCOの酸化を促進し、 NO_x の還元効率を向上させるものである。従って、触媒層B中にカリウムを含有すると、カリウムが前記貴金属のHC及びCO酸化性能を低下させるため、当該触媒層Bには、カリウムを含有してはならない。

【0036】また特に、請求項3記載の排気ガス浄化用触媒に関して、従来は、例えばCu担持ゼオライト触媒等の NO_x 浄化触媒と、Pt-ランタン触媒等の NO_x 吸収触媒はその特性上、前者は排気ガス中のHC/ NO_x 比が小さいと浄化作用が十分に得られず、また後者ではリーンで定常走行を行うと NO_x 吸収量が飽和に達してやがて吸収作用が無くなるという問題があり、幅広い運転条件下で NO_x を浄化することができなかった。従って、請求項3記載の発明では、排気ガスを一旦Cu担持ゼオライト触媒に接触させることで、後段の NO_x 吸収触媒の吸収作用を高めている。その吸収作用は、例えばCu担持ゼオライト触媒で NO_x 吸収に必要な NO_x の酸化が速やかに進行して NO_x 吸収材の働きを補助していることや、Cu担持ゼオライト触媒が NO_x 吸収に好都合なHC、 NO_x 、 O_2 濃度に変換していることなどが考えられる。

【0037】更に特に、請求項4記載の排気ガス浄化用触媒は、セリアがジルコニウム固溶型セリアであることにより、純粋なセリアを用いた場合と比べ、 NO_x 酸化性能および耐久性が高まり、優れた NO_x 吸収作用、耐久性を得る。

【0038】更に特に、請求項5記載の排気ガス浄化用触媒は、カリウム及びバリウムの含有量を各々上記したように限定することにより、ストイキ時の性能を確保しつつ NO_x 吸収性能を得る。

【0039】また、請求項6記載の排気ガス浄化用触媒の製造方法は、耐火性無機担体上に、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属を担持したアルミナ粉末と、当該貴金属の一部若しくは全部を担持したセリア粉末とを触媒担体にコートした後、焼成し、次いでこれにカリウム及びバリウムの金属塩の混合水溶液を含浸した後、焼成する製法とすることで、貴金属とセリアとの界面にカリウム及びバリウムが接し、バリウムとカリウムとが本来有する NO_x 吸収能力を十分に発揮できることとなる。

【0040】また、請求項7記載の排気ガス浄化用触媒の製造方法は、熱処理焼成温度を上記したように300

～600℃と限定することにより、貴金属の分散性を損なうことなく、触媒中に貴金属の均一な分散性をもたらす。

【0041】

【実施例】本発明を次の実施例及び比較例により説明する。

実施例1

10 活性アルミナ粉末に硝酸ロジウム(Rh)水溶液を含浸し、乾燥後400℃で1時間焼成して、Rh担持活性アルミナ粉末(粉末A)を得た。この粉末AのRh濃度は2.0重量%であった。活性アルミナ粉末にジニトロジ
20 アミン白金(Pt)水溶液を含浸し、乾燥した後、400℃で1時間焼成して、Pt担持活性アルミナ粉末(粉末B)を得た。この粉末BのPt濃度は4.0重量%であった。上記Rh担持活性アルミナ粉末(粉末A)108g、Pt担持活性アルミナ粉末(粉末B)531g、活性セリア粉末180g、活性アルミナ粉末81g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体(1.3L、400セル)に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/L-担体の材料を得た。当該コート層重量100g/L-担体の材料に、酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、400℃で1時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。

【0042】実施例2

30 カリウム及びバリウムの含有量を、各々酸化物に換算して10g/L、40g/Lとした以外は、実施例1と同様にして、排気ガス浄化用触媒を得た。

【0043】実施例3

硝酸ジルコニウムと硝酸セリウムの混合水溶液にアンモニアを添加し、得られた沈殿物を濾過し、乾燥した後、400℃で3時間焼成し、ジルコニウム固溶型セリア粉末(粉末C)を得た。当該ジルコニウム固溶型セリア粉末C中に含まれるジルコニウムの量は、金属モルに換算してZr/Ce=5/95であった。このジルコニウム固溶型セリア粉末Cを、実施例1の活性セリア粉末のかわりに用いた以外は、実施例1と同様にして、排気ガス浄化用触媒を得た。

【0044】実施例4

40 Zr/Ce=40/60のジルコニウム固溶型セリア粉末(粉末D)を実施例3と同様の方法で得、このジルコニウム固溶型セリア粉末Dを実施例1の活性セリア粉末のかわりに用いた以外は、実施例1と同様にして、排気ガス浄化用触媒を得た。

【0045】実施例5

50 活性セリア粉末にジニトロジアンミン白金(Pt)水溶

液を含浸し、乾燥した後、400℃で1時間焼成して、Pt担持活性セリア粉末（粉末E）を得た。この粉末EのPt濃度は2.0重量%であった。実施例1で得られたRh担持活性アルミナ粉末（粉末A）108gとPt担持活性アルミナ粉末（粉末B）351g、上記Pt担持活性セリア粉末（粉末E）180g、活性アルミナ粉末261g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（1.3L、400セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/Lー担体の材料を得た。当該100g/Lー担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、400℃で1時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。

【0046】実施例6

実施例5の活性セリア粉末のかわりに実施例3で得られたジルコニウム固溶型セリア粉末（粉末C）を用いた以外は、実施例5と同様にして、排気ガス浄化用触媒を得た。

【0047】実施例7

実施例1で得られたRh担持活性アルミナ粉末（粉末A）72gとPt担持活性アルミナ粉末（粉末B）348g、活性セリア粉末120g、活性アルミナ粉末60g、酢酸カリウム124g、酢酸バリウム428g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（1.3L、400セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量75g/Lー担体の下層触媒を得た。当該材料中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。実施例1で得られたRh担持活性アルミナ粉末（粉末A）108gとPt担持活性アルミナ粉末（粉末B）540g、活性セリア粉末180g、活性アルミナ粉末72g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液を上記75g/Lー担体に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成して上層触媒と下層触媒とを組み合わせるとータルでコート層重量125g/Lー担体の排気ガス浄化用触媒を得た。

【0048】実施例8

実施例7における上層触媒を下層触媒として、下層触媒を上層触媒として、コート層の上下を逆にする以外は、実施例7と同様にして、排気ガス浄化用触媒を得た。

【0049】比較例1

実施例1で得られたRh担持活性アルミナ粉末（粉末

A）108gとPt担持活性アルミナ粉末（粉末B）531g、活性アルミナ粉末261g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（1.3L、400セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/Lー担体の材料を得た。当該100g/Lー担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、400℃で1時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。

【0050】比較例2

実施例1で得られたRh担持活性アルミナ粉末（粉末A）108gとPt担持活性アルミナ粉末（粉末B）531g、活性セリア粉末180g、活性アルミナ粉末81g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（1.3L、400セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/Lー担体の排気ガス浄化用触媒を得た。

【0051】実施例9

活性アルミナ粉末にジニトロジアンミンパラジウム水溶液を含浸し、乾燥した後、400℃で1時間焼成して、Pd担持活性アルミナ粉末（粉末F）を得た。この粉末FのPd濃度は4.0重量%であった。当該Pd担持活性アルミナ粉末（粉末F）630g、活性セリア粉末180g、活性アルミナ粉末90g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（1.3L、400セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/Lー担体の材料を得た。当該100g/Lー担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、400℃で1時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。

【0052】実施例10

カリウム及びバリウムの含有量を、各々酸化物に換算して10g/L、40g/Lとした以外は、実施例9と同様にして、排気ガス浄化用触媒を得た。

【0053】実施例11

実施例3で得られたジルコニウム固溶型セリア粉末（粉末C）を実施例9の活性セリア粉末のかわりに用いた以外は、実施例9と同様にして、排気ガス浄化用触媒を得

た。

【0054】実施例12

実施例4で得られたジルコニウム固溶型セリア粉末(粉末D)を実施例9の活性セリア粉末のかわりに用いた以外は、実施例9と同様にして、排気ガス浄化用触媒を得た。

【0055】実施例13

活性セリア粉末にジニトロロジアンミンパラジウム水溶液を含浸し、乾燥した後、400℃で1時間焼成して、Pd担持活性セリア粉末(粉末G)を得た。この粉末GのPd濃度は4.0重量%であった。実施例9で得られたPd担持活性アルミナ粉末(粉末F)450g、上記Pd担持活性セリア粉末(粉末G)180g、活性アルミナ粉末270g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体(1.3L、400セル)に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/Lー担体の材料を得た。当該100g/Lー担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、400℃で1時間焼成して排気ガス浄化用触媒を得た。当該触媒15中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。

【0056】実施例14

実施例3で得られたジルコニウム固溶型セリア粉末(粉末C)を実施例13の活性セリア粉末のかわりに用いた以外は、実施例13と同様にして、排気ガス浄化用触媒を得た。

【0057】実施例15

実施例9で得られたPd担持活性アルミナ粉末(粉末F)420g、活性セリア粉末120g、活性アルミナ粉末60g、酢酸カリウム124g、酢酸バリウム428g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体(1.3L、400セル)に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量75g/Lー担体の下層触媒を得た。当該材料中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。実施例9で得られたPd担持活性アルミナ粉末(粉末F)630g、活性セリア粉末180g、活性アルミナ粉末90g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液を上記75g/Lー担体に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成して上層触媒と下層触媒とを組み合わせるとータルで125g/Lー担体の排気ガス浄化用触媒を得た。

【0058】実施例16

実施例15における上層触媒を下層触媒として、下層触媒を上層触媒として、コート層の上下を逆にする以外は、実施例15と同様にして、排気ガス浄化用触媒を得た。

【0059】比較例3

実施例9で得られたPd担持活性アルミナ粉末(粉末F)630g、活性アルミナ粉末270g、水900gを磁性ボールミルに加えて投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体(1.3L、400セル)に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/Lー担体の材料を得た。当該100g/Lー担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、400℃で1時間焼成して、排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して5g/L、20g/Lであった。

【0060】比較例4

実施例9で得られたPd担持活性アルミナ粉末(粉末F)630g、活性セリア粉末180g、活性アルミナ粉末90g、水900gを加えて磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体(1.3L、400セル)に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成してコート層重量100g/Lー担体の排気ガス浄化用触媒を得た。

【0061】実施例17

0.2mol/Lの硝酸銅水溶液5.2kgとゼオライト粉末2kgとを混合して攪拌した後、濾過する作業を3回繰り返した後、乾燥、焼成し、Cu担持ゼオライト粉末(粉末H)を得た。この粉末HのCu濃度は5%であった。このCu担持ゼオライト粉末(粉末H)810g、シリカゾル(固形分20%)450g、水540gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体(1.3L、400セル)に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成して、コート層重量300g/Lー担体のCu担持ゼオライト触媒を得た。このCu担持ゼオライト触媒を排気流れの上流側に、また実施例1で得られた触媒を下流側に配置した。

【0062】実施例18

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例2で得られた触媒を下流側に配置した。

【0063】実施例19

実施例17で得られたCu担持ゼオライト触媒を排気流

れの上流側に、また実施例 3 で得られた触媒を下流側に配置した。

【0064】実施例 20

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 4 で得られた触媒を下流側に配置した。

【0065】実施例 21

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 5 で得られた触媒を下流側に配置した。

【0066】実施例 22

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 6 で得られた触媒を下流側に配置した。

【0067】実施例 23

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 7 で得られた触媒を下流側に配置した。

【0068】実施例 24

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 8 で得られた触媒を下流側に配置した。

【0069】実施例 25

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 9 で得られた触媒を下流側に配置した。

【0070】実施例 26

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 10 で得られた触媒を下流側に配置した。

【0071】実施例 27

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 11 で得られた触媒を下流側に配置した。

【0072】実施例 28

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 12 で得られた触媒を下流側に配置した。

【0073】実施例 29

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 13 で得られた触媒を下流側に配置した。

【0074】実施例 30

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 14 で得られた触媒を下流側に配置した。

【0075】実施例 31

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 15 で得られた触媒を下流側に配置した。

【0076】実施例 32

実施例 17 で得られた Cu 担持ゼオライト触媒を排気流れの上流側に、また実施例 16 で得られた触媒を下流側に配置した。

【0077】上記実施例 1～32 及び比較例 1～4 の触媒組成を次の表 1 及び 2 に示す。

【表 1】

	貴金属 (g/L)			添加材 (酸化物 g/L)		
	Pt	Rh	Pd	Ce	K	Ba
実施例 1 実施例 17	1.18	0.24	—	20.0	5.0	20.0
実施例 2 実施例 18	1.18	0.24	—	20.0	10.0	40.0
実施例 3 実施例 19	1.18	0.24	—	20.0 (*1)	5.0	20.0
実施例 4 実施例 20	1.18	0.24	—	20.0 (*2)	5.0	20.0
実施例 5 実施例 21	1.18	0.24	—	20.0	5.0	20.0
実施例 6 実施例 22	1.18	0.24	—	20.0	5.0	20.0
実施例 7 実施例 23	1.18	0.24	—	20.0	5.0	20.0
実施例 8 実施例 24	1.18	0.24	—	20.0	5.0	20.0
実施例 9 実施例 25	—	—	2.83	20.0	5.0	20.0
実施例 10 実施例 26	—	—	2.83	20.0	10.0	40.0
実施例 11 実施例 27	—	—	2.83	20.0 (*1)	5.0	20.0
実施例 12 実施例 28	—	—	2.83	20.0 (*2)	5.0	20.0
実施例 13 実施例 29	—	—	2.83	20.0	5.0	20.0
実施例 14 実施例 30	—	—	2.83	20.0	5.0	20.0
実施例 15 実施例 31	—	—	2.83	20.0	5.0	20.0
実施例 16 実施例 32	—	—	2.83	20.0	5.0	20.0

(*1) : Zr/Ce 重量比 = 5/950

【表 2】

	貴金属 (g/L)			添加材 (g/L)		
	Pt	Rh	Pd	Ce	K	Ba
比較例 1	1.18	0.24	—	—	5.0	20.0
比較例 2	1.18	0.24	—	20.0	—	—
比較例 3	—	—	2.83	—	10.0	10.0
比較例 4	—	—	2.83	20.0	—	—

【0078】試験例 1

前記実施例 1～32 及び比較例 1～4 の触媒及び触媒シ

システムについて、以下の条件で初期及び耐久後の触媒活性評価を行った。活性評価には、自動車の排気ガスを模したモデルガスを用いる自動評価装置を用いた。

【0079】耐久条件

エンジン4400ccの排気系に触媒を装着し、600℃で、50時間運転して耐久を行った。

【0080】評価条件

触媒活性評価は、排気量2000ccのエンジンの排気系に各触媒を装着し、 $A/F=14.6$ （ストイキ状 *

*態）で30秒間、その後 $A/F=22$ （リーン雰囲気）で30秒間の運転を1サイクル行ない、各々平均転化率を測定し、この $A/F=14.6$ （ストイキ状態）の場合の平均転化率と $A/F=22$ （リーン雰囲気）の場合の平均転化率とを平均してトータル転化率とした。この評価を初期及び耐久後に各々行ない、触媒活性評価値を以下の式により決定した。

【数1】

$$\text{NOx転化率(\%)} = \frac{[\text{触媒層入口NOx濃度}] - [\text{触媒層出口NOx濃度}]}{[\text{触媒層入口NOx濃度}]} \times 100$$

（HC、COも同様）

【0081】トータル転化率として得られた触媒活性評価結果を表3～5に示す。比較例に比べて実施例は、触媒活性が高く、後述する本発明の効果を確認することが

できた。

【表3】

	初期転化率 %			耐久後転化率 %		
	HC	CO	NOx	HC	CO	NOx
実施例 1	91	100	90	92	97	62
実施例 2	88	99	93	91	97	65
実施例 3	93	100	92	95	99	67
実施例 4	93	100	92	96	99	66
実施例 5	92	100	92	93	97	64
実施例 6	96	100	95	95	99	68
実施例 7	92	100	91	93	98	63
実施例 8	91	100	91	93	98	63
比較例 1	88	100	87	89	95	59
比較例 2	90	100	89	90	96	50

【表4】

	初期転化率 %			耐久後転化率 %		
	HC	CO	NOx	HC	CO	NOx
実施例 9	95	100	93	96	99	65
実施例 10	89	99	93	94	98	67
実施例 11	93	100	95	95	99	68
実施例 12	95	100	96	96	99	68
実施例 13	95	100	96	95	97	65
実施例 14	97	100	96	95	99	70
実施例 15	94	100	93	94	98	65
実施例 16	94	100	93	95	98	63
比較例 3	89	100	89	89	95	56
比較例 4	90	100	89	90	96	51

【表5】

	初期転化率 %			耐久後転化率 %		
	H C	C O	N O x	H C	C O	N O x
実施例 17	92	100	98	92	98	77
実施例 18	90	100	98	91	98	79
実施例 19	93	100	96	95	99	78
実施例 20	93	100	96	96	99	80
実施例 21	92	100	97	93	97	82
実施例 22	96	100	96	95	99	83
実施例 23	92	100	98	93	98	79
実施例 24	91	100	98	94	98	79
実施例 25	96	100	97	90	95	79
実施例 26	94	100	95	93	96	80
実施例 27	95	100	96	96	99	80
実施例 28	95	99	96	95	98	80
実施例 29	96	100	98	96	99	83
実施例 30	98	100	96	95	99	86
実施例 31	95	100	96	95	98	80
実施例 32	95	100	97	95	98	80

【0082】

【発明の効果】請求項1記載の排気ガス浄化用触媒は、貴金属と、セリアと、バリウム及びカリウムを含有し、貴金属の一部又は全部がセリアに担持されていることにより、従来の触媒では十分な活性が得られないリーン雰囲気下におけるNO_x浄化性能を、NO_x吸収に必要なNO_x酸化反応を向上させることにより高めることができ、かつ耐久後においても三元触媒としての機能を十分に発現することができる。

【0083】請求項2記載の排気ガス浄化用触媒は、更に貴金属担持層と、請求項1記載の触媒層とを、任意に上下に組み合わせることにより、前記効果に加えて更にH₂C及びCO活性を向上させることができる。

【0084】請求項3記載の排気ガス浄化用触媒は、排気気流に対して上流側に銅担持ゼオライト含有触媒を、下流側に上記請求項1又は2記載の触媒を配置することにより、上記効果に加えて、更にNO_x吸収作用を高めることができる。

【0085】請求項4記載の排気ガス浄化用触媒は、更にセリアをジルコニウム固溶型セリアとすることにより、上記効果に加えて、NO_x酸化性能及び耐久性を更に高めることができる。

【0086】請求項5記載の排気ガス浄化用触媒は、更にカリウム及びバリウムの含有量を特定することにより、上記効果に加えて、ストイキ時の性能も確保されることとなる。

【0087】請求項6記載の排気ガス浄化用触媒の製造方法は、上記説明した工程を経ることにより、貴金属とセリアとの界面にカリウム及びバリウムが十分に接することができるので、これによりNO_x吸収能力を十分に発揮できる請求項1記載の排気ガス浄化用触媒を簡便に製造することができる。

【0088】請求項7記載の排気ガス浄化用触媒の製造方法は、更に熱処理焼成温度を限定することにより、上記効果に加えて、排気ガス浄化用触媒中への貴金属の分散を、更に均一にすることができる。

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